Structure and Morphology of Nanostructured Zinc Oxide Thin Films Prepared by Dip- *vs*. Spin-Coating Methods

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In this study, we use dipping and spinning methods to coat glass slides with sol-gel ZnO thin films, composed of zinc acetate dihydrate, monoethanolamine (MEA), de-ionized water and isopropanol. The effect of the annealing temperature on the structural morphology and optical properties of these films is investigated. These ZnO films were preheated at 275 °C for 10 min and annealed either at 350, 450 or 550 °C for 60 min. As-deposited films, formed by amorphous zinc oxide-acetate submicron particles, are transformed into a highly-oriented ZnO after thermal treatment. The surface morphology, phase structure and optical properties of the thin films were investigated by scanning electron microscopy, X-ray diffraction (XRD) and optical transmittance. Both techniques produced nanostructured ZnO thin films with well-defined orientation. The annealed films were transparent in the visible range with an absorption edge at about 375 nm and a transmittance of ca 85-90% with an average diameter of 40 nm. XRD results show the film was composed of polycrystalline wurtzite, with a preferential *c*-axis orientation of (002) and a single sharp XRD peak at 34.40, corresponding to the hexagonal ZnO. The grain size is increased by the annealing temperature. Both coating techniques create sol-gel ZnO films with the potential for application as transparent electrodes in optic and electronic devices.

Keywords: Nanostructure, Sol-gel, Thin film, Spin coating, Dip coating, ZnO

INTRODUCTION

Current interest in the creation of nanostructures on surfaces by a variety of self-organizing techniques has focused on their application in sensors and molecular electronics. Such nanostructures exhibit novel electrical, mechanical, chemical and optical properties, due to their one dimensional (1D) surface confinement effects. These 1D objects help in understanding certain basic physics-related phenomena of low-dimension systems that will help to form the basis of next-generation high-performance nanodevices.

Along these lines, the sol-gel process has the unique

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advantage of allowing the preparation of materials of the same composition, such as silica, in markedly different physical forms, fibers, coatings, and monoliths, just by varying a few experimental conditions. Sol-gel chemistry has recently evolved into a general and powerful approach for preparing inorganic materials [1-5].

ZnO thin films are important materials [6], due to their wide applicability in photoluminescence, transparent semi-conductors [7], photocatalysts, piezoelectricity [8], gas sensors [9] UV light emitting devices [10,11], varistors [12] and optical devices [13]. There are various methods for preparing ZnO thin films including physical vapor deposition [14], chemical vapor deposition (CVD) [15], spray pyrolysis, sputtering [16,17] and pulsed laser deposition (PLD) [18], as

well as the ink-jet printing [19], basic erosion [20] and sol-gel methods [21-28]. The important advantages of sol-gel processing, for the purpose of conventional thin film deposition, are chemical composition control, low-temperature annealing and homogeneity of the sol solution. These advantages make sol-gel processing a very appealing and commercially-favorable method for ZnO thin film preparation.

For the growth ZnO thin films, it is important to control the orientation for each application. ZnO films with (002) orientation are typically observed for films grown by various methods because the *c*-plane perpendicular to the substrate is the most densely packed and thermodynamically favorable plane in the wurtzite structure. This (002) orientation is especially important for piezoelectric applications, whereas the (100) orientation, with its relatively larger grain size, is preferred for transparent conductive oxide (TCO) applications. Precursor materials and preparation conditions, especially the postannealing temperature, are known to affect the properties of sol-gel ZnO thin films.

Among the methods for creating ZnO films, atomic layer deposition (ALD) [29], which uses a surface reaction between the precursors, is known to produce high quality films with low structural imperfection. However, the ALD method, using diethyl zinc (DEZ) and water, favors the (100) orientation at low deposition temperatures [30]. The preferred (002) orientation of the ZnO film fabricated by ALD can be obtained at a substrate temperature above 400 ℃.

Kaiya *et al*. recently reported the ALD growth of ZnO film, with an intense diffraction peak assigned to the (002) reflection, by using $ZnCl_2$ and O_2 as the precursors for Zn and O, respectively, at substrate temperatures higher than 450 ℃ [31]. Chaisitsak *et al*. reported that the orientation of ZnO films grown by ALD is strongly dependent on the DEZ flow rate at a substrate temperature of 165 ℃ [32]. Considering that ALD is known to be rather insensitive to the precursor flux, that result was quite interesting. Although the effect of the substrate temperature on the crystal growth direction of ALD-grown ZnO films has been reported, detailed studies on other factors determining film growth direction are lacking. In this experiment, we have investigated the effects of oxygen precursor on ZnO film growth by the ALD method.

In our earlier works [33-35] we have reported the production, characterization and application of nanostructured

metal oxide (TiO2 and ITO) thin films. In our recent work [36] we reported the glass plate-supported nanostructure ZnO thin films deposited by sol-gel spin coating. However, the transmittance of films prepared by the spin-coating technique was low.

In the present study we have made an attempt to study the morphology, texture and transmittance of the ZnO films and their dependence on the coating technique. Therefore dip-coating was employed in preparing nanostructured ZnO thin film, which modifies the surface and leads to higher transmittance and more uniform films compared to spin coating.

EXPERIMENTAL

Preparation of Sol

All the chemicals were of analytic grade, purchased from the Merck Company and were used without further purification. To prepare the sol solution, 3.10 g zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O:ZnAc_2.2H_2O$), 0.86 g mono-ethanolamine (MEA) and adequate deionized water were added to 15 ml isopropanol alcohol, and then heated to 65 ℃ with continuous stirring for 1 h. The sol-gel coating was typically made one day after the preparation of the sol solution, and the molar ratio of MEA to zinc acetate was maintained at 1:1.

Film Deposition

A glass microscope slide (75 mm × 25 mm × 1 mm) was cleaned in dilute HCl solution and ethanol. Film deposition was carried out in air at room temperature by the dip-coating method with a controlled withdrawal speed of 1 cm min⁻¹. ZnO films were also spin-coated onto the glass substrate, during which the spinner reached 3000 rpm after 5 s and maintained at that speed for 40 s. For each layer, the films were preheated at 275 ℃ for 10 min and postheated at 350, 450 or 550 ℃ for 1 h. The deposition was repeated five times to obtain five-layered films.

Characterization Techniques for Thin Films

The structure and crystal size were determined by XRD using a Bruker D8 advanced X-ray diffractometer (Cu k$_\alpha$ radiation, λ = 1.54 Å, scan rate 0.03 2θ s⁻¹). The transparency

of the films was measured using a CECIL-CE7500 ultraviolet-visible spectrophotometer. The surface of the films was observed by SEM using a Philips XL30 electron microscope.

RESULTS AND DISCUSSION

There are many factors affecting the crystallization behavior of these films, such as the properties of stabilizers, like MEA, the duration and temperature of reflux, molar ratio of the starting material, and the type of substrate.

Stability of Sol

The sol system requires a delicate balance. Increasing the water content and dilution of the sol system and decreasing the duration of reflux may cause the sol to gel immediately. MEA and water are added to keep the sol solutions stable and clear for 60 days. The solution is refluxed until it is clear and homogeneous.

Structure and Morphology

The morphology and texture of ZnO thin films made by the sol-gel process are affected by solvent, preheating and postheating temperatures, concentration of sol, substrate and coating procedure. We found that the nanostructure of the ZnO thin film had a high degree of c-axis orientation, which influenced the optical and electrical properties of the coating. The thermodynamics of the nucleation and crystal growth of the ZnO thin films indicate the occurrence of a transformation from the amorphous to the crystalline state. This crystalline growth of predominately c-axis orientation depends on the surface energies of the film and the glass substrate and the interfacial energy between them [37-39]. In the crystal growth, a fast growing plane generally tends to disappear leaving behind slower growing planes with lower surface energies. Therefore, the (001) and (101) planes of ZnO thin film disappear during the growth, and the overall growth direction is perpendicular to the substrate [40-42].

Figures 1 and 2 show SEM images revealing the nanostructure of the ZnO thin film, with an average grain size of approximately 40 nm and a porous granular surface.

Figures 3 and 4 show the XRD pattern of the five-layered ZnO thin film on the glass substrate by spin and dip coating, respectively. The XRD patterns of the thin films have lower
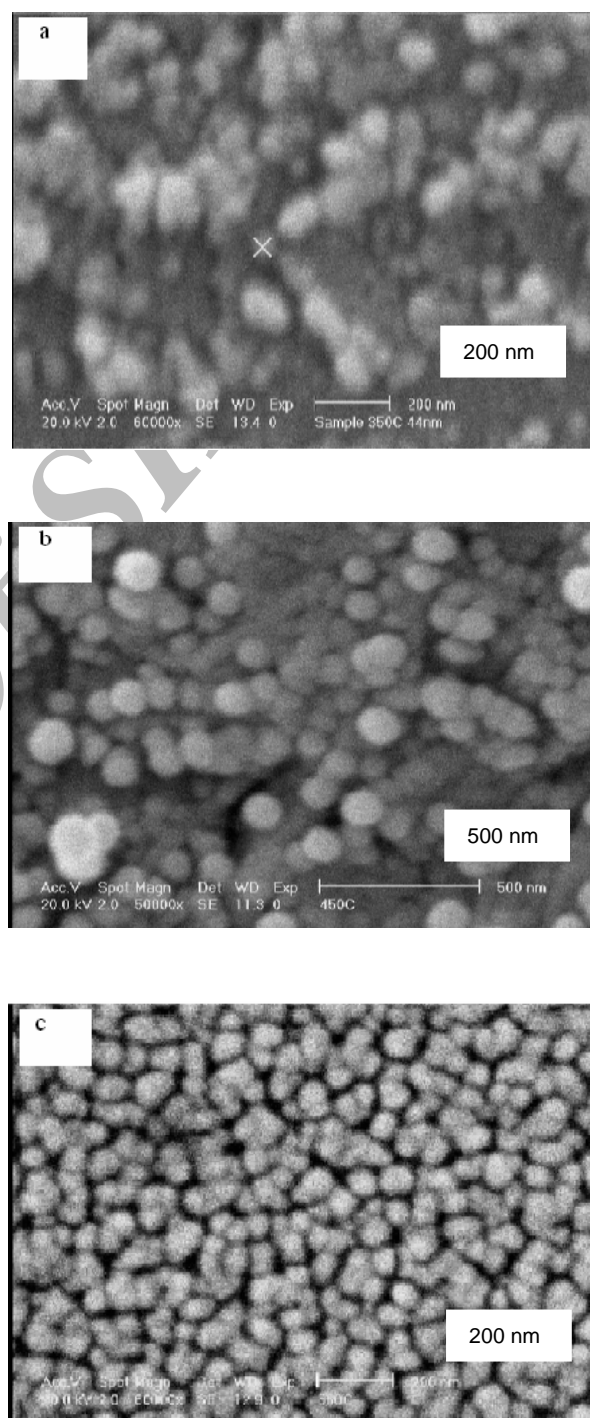

Fig. 1. SEM images of the ZnO thin film on a glass substrate by a dip coating (5 layers) preheated at 275 ℃ for 10 min and postheated for 60 min at 350 ℃ (a), 450 ℃ (b) or 550 ℃ (c).
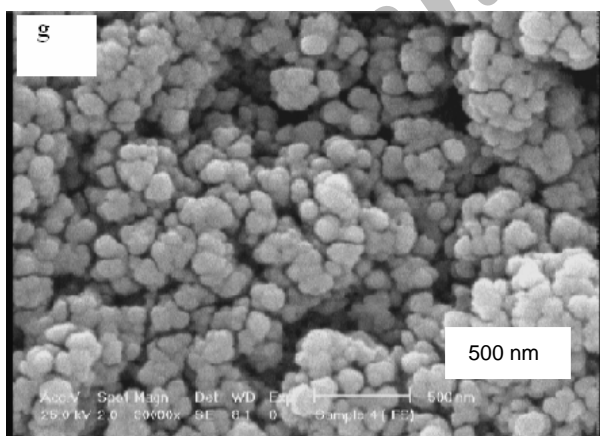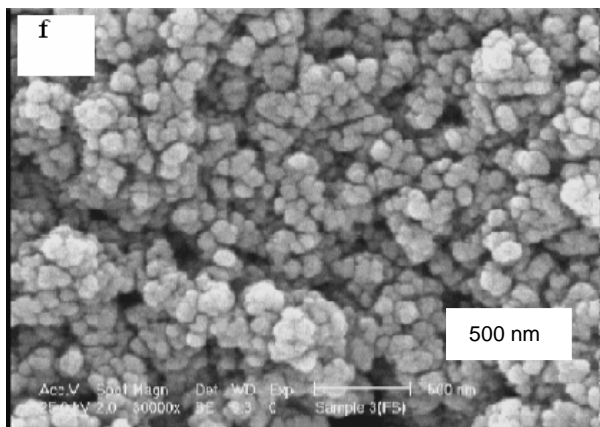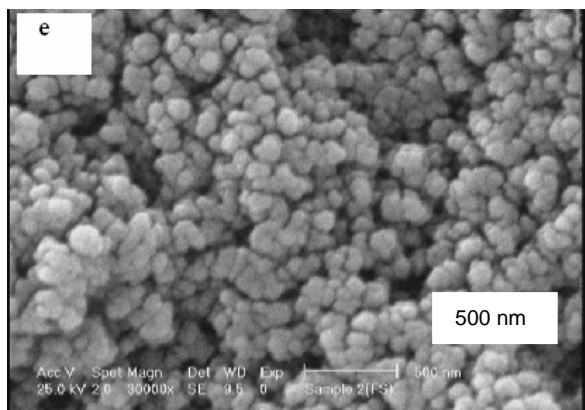
Fig. 2. SEM images of the ZnO thin film on a glass substrate by spin-coating (5 layers) preheated at 275 ℃ for 10 min and postheated for 60 min at 350 ℃ (a), 450 ℃ (b) or 550 ℃ (c).
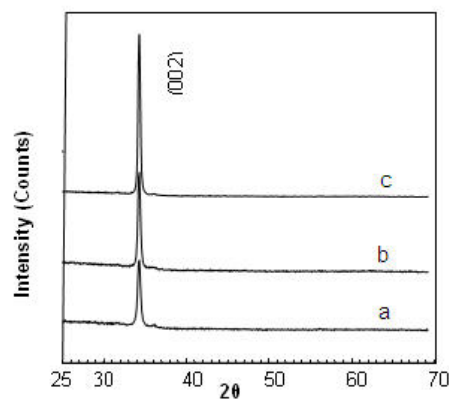

Fig. 3. XRD pattern of the ZnO thin film on a glass substrate by dip-coating (5 layers) preheated at 275 ℃ for 10 min and postheated for 60 min at different temperatures.
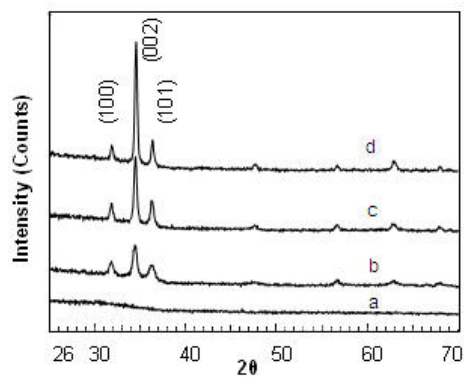

Fig. 4. The XRD pattern of the ZnO thin film on a glass substrate by spin-coating (5 layers) preheated at 275 ℃ for 10 min and postheated for 60min at three different temperatures.

intensity and higher FWHM (full width at half maximum) than those of ZnO powder in Fig. 5. Furthermore, XRD shows that the films have a wurtzite structure with a *c*-axis that is predominantly (002) oriented, when crystallized at higher temperatures (highest at 550 ℃). The growth of ZnO thin films with a (002) orientation is kinetically preferred, reflecting that the highest density of Zn atoms is found along the (002) plane [43].

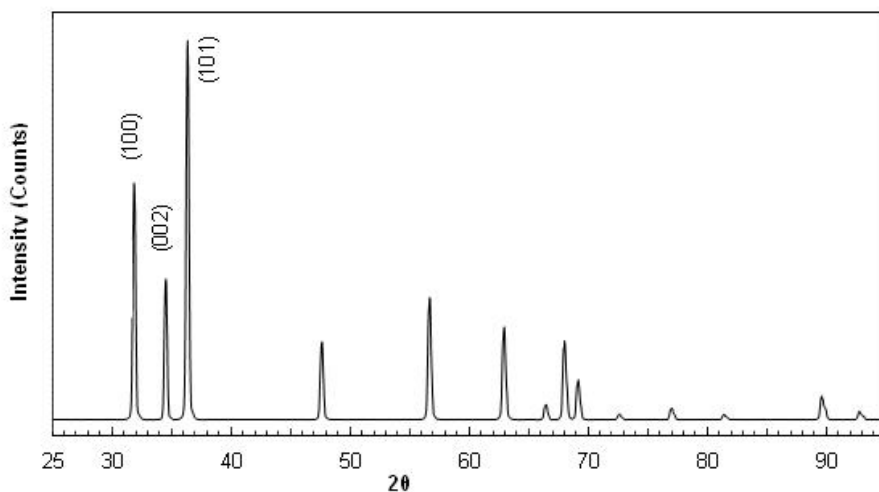Optical transmittance of ZnO thin films preheated at 275 ℃ for 10 min and postheated at 350, 450 and 550 ℃ for 1 h
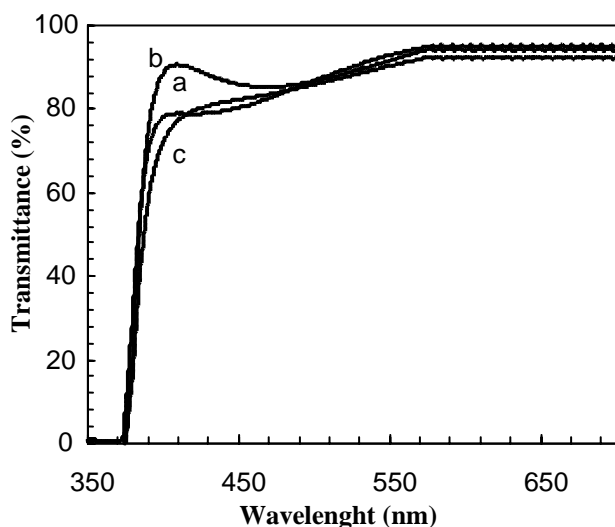
Fig. 5. XRD pattern of ZnO powder.

Fig. 6. Optical transmittance of ZnO thin films prepared by dip coating (5 layers) and postheated at 350 ℃ (a), 450 ℃ (b) or 550 ℃ (c).
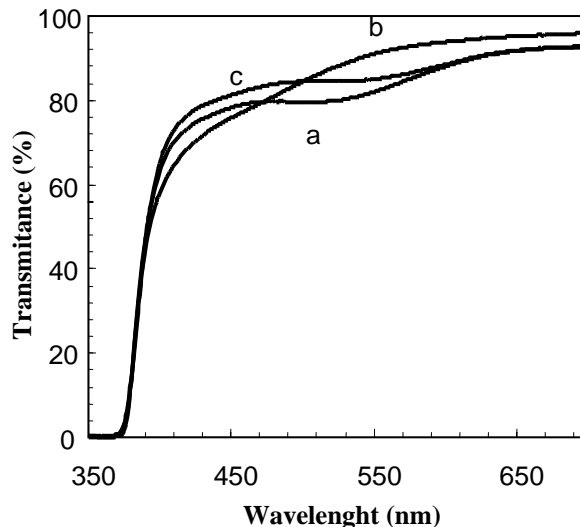

Fig. 7. Optical transmittance of ZnO thin films prepared by spin-coating (5 layers) and postheated at 350 ℃ (a), 450 ℃ (b) or 550 ℃ (c).

are shown in Figs. 6 and 7. The absorption at wavelengths around 370 nm corresponds to an electronic transition beyond the band gap of the crystalline ZnO (3.2 eV). An increase in the transmittance of the ZnO thin film is observed after the annealing treatment due to the release of hydroxide species remaining in the film. Also shown in Figs. 6 and 7, the transmittance of films prepared by the spin-coating technique

is lower than that of the films prepared by dip-coating. In order to explain this difference, we note that film thickness and porosity affects the transmittance [45]. As shown in Figs. 1 and 2, thin films prepared by spin coating have a more porous surface and large cluster grains. In contrast, thin films prepared by dip coating have lower porosity and small

clusters. Therefore, the morphology and texture of the films made by the sol-gel process appear to be dependent on the coating technique.

The size of the ZnO crystals in the films was calculated by Scherrer's formula: $D = 0.9\lambda/\beta\cos\theta$ [44], where D is the grain size, λ (1.548 Å) the wavelength of X-rays used, and β and θ are the FWHM and Bragg diffraction angle of the XRD peak, respectively. The average-sized crystals of the ZnO in the films that anneal at 350, 450 and 550 ℃ are about 19, 22 and 24 nm, respectively, for the dip coating technique. For the spin coating, same parameters are approximately 16, 23 and 25 nm, respectively. It was observed that the *c*-axis orientation improves as the grain size increases, as is indicated by an increase in intensity of the (002) peak and the decrease in the FWHM height with an increase in the annealing temperature.

CONCLUSIONS

The goal of sol-gel processing is to provide nanoscale control over the structure of a material from the earliest stages of processing. For pure material powders, thin films, fibers, and even monoliths this goal has been achieved. Transparent nanostructured ZnO thin films on glass substrates were prepared by sol-gel method using dip-coating and spin techniques for film deposition. The films produced by both techniques were found to be highly *c*-axis oriented and the transmittance was higher than 85% in the visible range. The present work represents an alternative approach to previous studies and describes the synthesis and size of the ZnO nanocrystal using solutions with few additives that yield stable sols and homogeneous layers. Using zinc acetate and MEA as starting compounds along with the proper annealing conditions, we obtained high-quality pure coatings with a structure suitable to produce stable guest oxide nanocrystals. The thin films were characterized by XRD, SEM and ultraviolet-visible spectrophotometry, which indicate that sol-gel ZnO films have potential applications such as catalyst and transparent electrodes in opto-electronic devices.

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